Proton transport for fuel cells

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International efforts in fuel cell materials research have been largely driven by the need to develop benign energy technologies. As is widely recognized, fuel cells have the potential to convert chemical energy into electrical energy at exceptionally high efficiencies and with almost undetectable emissions of regulated pollutants. As electrolytes for fuel cells, proton conducting materials offer an important advantage over their counterparts based on mobile anions (*i.e.*, OH^-, O^{2-}, CO_3^{2-}) for operation on hydrogen; because H_2O is produced at the cathode rather than the anode, hydrogen fuel is not diluted during operation as occurs in other fuel cell types. However, while fuel cells based on proton conducting membranes are well-suited to hydrogen fuel, they are by no means limited to this particular energy carrier. Thus, research in proton conductors for fuel cells remains vibrant, despite a thoughtful re-evaluation of the global commitment to a hydrogen energy economy.

Beyond the technological significance of proton conducting materials, the very nature of a proton – a bare atomic nucleus – renders it unique amongst ionic species. It is mobile in a broad range of materials, from acid-functionalized polymers, to hydrated oxides, to oxyanion acid salts containing structural protons. In the solid state it typically resides within the electron cloud of the anions to which is it bound (normally oxygen in proton conductors) and its structural and dynamical characteristics can be probed by a host of techniques from nuclear magnetic resonance spectroscopy and neutron scattering methods, to isotope effect measurements and computational studies. In parallel with advanced characterization, synthesis of proton conducting materials, both new and known, has become an increasingly sophisticated endeavor. This is particularly true of polymeric systems, in which research has evolved from a hit and miss, brute-force approach of synthesizing and then characterizing different acid-functionalized polymers to more sophisticated strategies that focus on morphologcial manipulation and control, especially at the nanoscale. As the synthesis of pure proton conductors matures, efforts are being directed towards the development of materials with multiple mobile carriers (protons plus "x") to create new functionalities. The papers in this themed issue of *Journal of Materials Chemistry* exemplify nicely these recent trends and present key advances in fuel cell materials research. Thus, the results herein provide the reader with an excellent "snapshot" of state-of-the-art research within the protonics community.

Amongst the polymer papers, three in this issue deal with new membrane morphologies for moderate temperature fuel cells (as candidates with enhanced properties to replace DuPont's Nafion perfluorosolfonic acid membranes). Layer-by-layer (LbL) assembly methods offer many possibilities for tuning the structure, composition, and thickness of next-generation proton conducting fuel cell membranes. Thus, Hammond and co-workers at MIT show that one can alter the ionic crosslink density and properties of LbL membranes composed of alternating nm-thick layers of poly(diallyl dimethyl ammonium chloride) and sulfonated poly(2,6,-dimethyl 1,4-phenylene oxide) by adjusting the ionic strength of the assembly solution. The highest ionic conductivity (7.0×10^{-2} S cm^{-1} at 25 °C) reported to date for any LbL membrane was achieved by optimizing the membrane fabrication conditions. The use of block copolymers for fuel cell membranes has long been an attractive idea, where tunable phase-separated polymer morphologies are generated to promote proton conductivity while limiting water uptake. Hickner's group at Penn State presents their recent results on such a system, where triblock copolymer films are examined. The effects of mid-block sulfonation degree and hydrophobic endblock composition on the block copolymer domain size, the degree of self-assembly, and the proton conductivity and water swelling properties of solvent cast membranes is quantified. Some triblock compositions generated promising preliminary results, with a membrane conductivity exceeding that of Nafion® at 30 °C for relative humidities greater than 65%. An alternative to self-assembled block copolymer systems is presented by Pintauro *et al.* in their paper on nanofiber composite proton conducting membranes. In this study, a 3-D interconnecting network of electrospun proton-conducting perfluorosulfonic acid polymer nanofibers is created and then the interfiber voids are filled with an inert/impermeable (uncharged) polymer to provide mechanical strength, gas barrier properties, and water swelling control. In such a forced assembly system, the role of the mechanical support polymer is decoupled from that of the proton conducting material. Membranes made with 3M Corporation ionomer nanofibers and Norland Optical Adhesive as the inert polymer matrix material exhibited a higher proton conductivity than that of commercial Nafion® at 80 °C and relative humidities between 50% and 80%, with low water swelling and improved mechanical properties.

Two papers in this themed issue deal with new polymeric proton conducting materials for anhydrous fuel cell operation above room temperature. Matsuda *et al.*, fabricated and tested a series of polybenzimidazole (PBI) films that were loaded with heteropoly acid (HPA), as a potential replacement for acid-doped PBI. Inorganic–organic composite membranes, containing either phosphotungstic acid or silicotungstic acid, were prepared and evaluated for different HPA loadings. Optimized films exhibited a high proton conductivity (1.91×10^{-2} S cm^{-1} at 160 °C under anhydrous conditions) and performed well in hydrogen/air fuel cell tests. Roy and co-workers in their paper pursued a different strategy, where a liquid crystalline phenylsulfonic acid compound was examined as a possible membrane material that conducts protons under non-humidified conditions. In its *smectic A* liquid crystal state, the proton conductivity of 4-(octadecyloxy)phenylsulfonic acid at 80 °C in dry

nitrogen was very high (1.0×10^{-2} S cm^{-1}), as compared to a conductivity of 1.5×10^{-7} S cm^{-1} for the same material in a solid powder state. X-Ray experiments and molecular modeling studies suggested that proton conducting liquid crystals posses a lamellar structure composed of bilayer stacks of phenylsulfonic acid. The authors would like to use this compound for high temperature anhydrous fuel cell operation, but first they must find a method of stabilizing the morphology above the liquid crystal temperature range.

Direct methanol fuel cells (DMFCs) are a viable alternative to fuel cells powered by hydrogen, especially for portable power applications. The membrane in such devices requires a unique and seemingly contradictory set of properties: high proton conductivity (which requires highly hydrophilic polymer domains) and low methanol crossover (which is best achieved if the membrane hydrophilicity is minimized). The two papers in this themed issue that deal with DMFC membranes take a somewhat similar approach: add a sufficient number of protogenic groups to the polymer for high conductivity and then crosslink the polymer to minimize swelling in aqueous methanol solutions (where reduced swelling translates into lower methanol permeability). Thus, Wang *et al.* in their paper describe the synthesis and properties of an amino-terminated copolymer, with varying amounts of perfluorosulfonic acid moieties, that was crosslinked with a triisocyanate agent. By proper adjustment of polymer ion-exchange capacity, crosslinked membranes with exceptionally low methanol permeability and reasonable proton conductivity were fabricated. In the second DMFC paper, Na and co-workers report on a new class of hybrid membranes composed of crosslinked sulfonated poly(ether ether ketone), with an ion-exchange capacity in the range of 1.18–1.55 mmol g^{-1}, that were loaded with 10–40 wt% heteropoly acid (phosphotungstic acid). The approach yields materials with an attractive combination of sufficient conductivity, unusually low swelling (less than 20% at 80 °C), good mechanical properties, and methanol permeability was is order of magnitude lower than that in commercial Nafion.

The last polymeric proton conductor paper to discuss for this themed issue is the molecular modeling study by Paddison *et al.* Over the years, molecular simulations have provided valuable insights into how acid-functionalized polymers interact with water and how proton conducting membranes function at high and low water contents, especially with regards to perfluorosulfonic acid polymers membranes. In their present paper, Paddison and co-workers have chosen to model water and protons in a single-walled carbon nanotube functionalized with $-CF_2SO_3H$ groups, as an ideal hydrophilic channel in a minimally hydrated (hypothetical) perfluorosulfonic acid membrane. *Ab initio* molecular dynamic simulations revealed that dissociation of the acidic proton increased with increasing density of sulfonic acid groups up to a limit (after which there was proton trapping) and the presence of fluorine atoms on the nanotube wall affected the hydrogen bonding network of water, where the sulfonic acid groups had less tightly bound water and an enhanced proton dissociation.

Amongst proton conducting oxides, perhaps trivalent doped barium zirconate and derivatives thereof have received the greatest attention in recent years due to their combined characteristics of high inherent (bulk) proton conductivity, chemical stability, and mechanical robustness. The papers presented here tackle the difficult problems of elucidating transport mechanisms as they relate to defect chemistry and dynamics and of high grain boundary impedance. In a computational study, Islam and co-workers predict proton trapping in trivalent doped $BaPrO_3$ and $BaZrO_3$. In the series M^{3+} = Sc, In, Yb, Y and Gd, trapping was most severe for Sc, consistent with experimental observations that Sc-doped $BaZrO_3$ has low proton conductivity. They furthermore find that trapping is more pronounced for $BaPrO_3$ than $BaZrO_3$. A tantalizing prediction from this study is that Gd-doped barium zirconate, which has received little attention, should have higher conductivity than the widely studied Y-doped material. In a comprehensive NMR study of Sc-doped $BaZrO_3$, Grey and co-workers provide a somewhat different picture of defect distributions than the computational predictions. These authors find that, prior to hydration, Sc and O are randomly distributed so long as the Sc content is sufficiently below its solubility limit. Upon hydration, they observe, at most, a slight tendency of the protonic defect to order nearby a scandium ion. As an alternative to trapping effects, these authors suggest that the O–H dipole reorientation barrier may be inherently high for Sc doped barium zirconate due to strong hydrogen bonding, giving rise to the observed low conductivity.

Yugami and co-workers have explored the origins of high grain boundary impedance in Y and Gd doped barium zirconate. Transmission electron microscopy reveals the grain boundaries be free of impurity phases, but slightly enhanced in dopant concentration relative to the bulk. Furthermore, the grain boundary impedance was observed to decrease with increasing measurement voltage (whereas the bulk properties remained constant). These results provide evidence (though not conclusive) that the high impedance is due to space charge effects. The grain boundary barrier height is observed to decrease with increasing yttrium concentration and upon replacing Y with Gd, suggesting strategies for enhancing transport across grain boundaries. The poor transport properties across the grain boundaries of doped barium zirconate has been a recognized obstacle for several years, a problem exacerbated by inherently poor grain growth leading to a high number density of grain boundaries. It the past few years it has become well recognized that sintering aids such as ZnO, NiO and CuO enhance grain boundary mobilities, thereby lowering the temperatures required for good densification and enhancing grain growth. Tong *et al.* provide a careful study of the mechanism by which NiO in particular aids in the processing of yttrium doped barium zirconate. Following a reactive sintering procedure, they find that the intermediate, transient compound, BaY_2NiO_5, plays a major role in densification and grain growth.

While proton transport in doped perosvkites is generally considered attractive at temperatures in the range of 400 to 600 °C (below 400 °C the mobility is low and above 600 °C dehydration occurs), several 'hard' materials display high conductivity at lower temperatures, competing, in some sense, with the high temperature

polymers. In a comprehensive feature article, Sinistyn provides a review of the pressure-temperature phase behavior in $MeHAO_4$ compounds (Me = Cs, Rb, NH_4 and A = S, Se, and all combinations except NH_4HSeO_4 are explicitly discussed). While each material has, of course, distinct phase behavior, Sinistyn creates an integrated approximate picture in which pressure and ion size are equivalent and each of the compounds displays so-called superprotonic conductivity (in a phase with orientationally disordered oxyanion groups) under the appropriate thermodynamic conditions. Chemically related to these solid acids are metal pyrophosphates, MP_2O_7 materials. Proton incorporation is attributed to a hydration reaction, similar that of the oxides, but with due recognition of a high electronic hole concentration. Hibino reports a study of new compositions in this class, $Sn_{1-x}Al_xP_2O_7$, as well as reviewing the technological developments in fuel cell preparation and testing.

An entirely different approach is adopted by Kim, who has induced ambient temperature proton conduction in yttria-stabilized zirconia through nanostructuring. At temperatures below ~180 °C, conductivity monotonically increases with decreasing grain size (in the range 17 to 100 nm) and with increasing water partial pressure, consistent with high proton transport along grain boundaries. Bridging the polymeric and non-polymeric materials is the work of Yamaguchi, who has prepared nanoparticulate zirconium phosphate, zirconium sulfophenyl-phosphonate, and zirconium sulfate materials as precursor components for polymer–inorganic hybrids. The mild synthesis conditions set the stage for *in situ* conversion of zirconium oxide to the material of interest in the presence of the polymer of interest, while the reported conductivities even in the absence of any polymer, are already attractive.

In any operational fuel cell, the proton conducting electrolyte is accompanied by electrodes, which in some regards must meet a higher set of functional requirements than the membrane. It is commonly recognized that electrode materials that transport both ionic and electronic species can broaden the physical zone for the electrochemical reactions, thereby enhancing activity. Tricoli describes a sol–gel route for synthesizing high surface area WO_3 and controlling the relative magnitudes of protonic and electronic conductivities. Specific surface areas of ~100 $m^2\ g^{-1}$ and pore diameters of 5–10 nm are readily achieved, attractive values for fuel cell electrodes. Haile and co-workers present a very different synthesis method for the preparation of multi-component electrodes for fuel cells based on CsH_2PO_4. The electrospray approach is demonstrated to yield high surface area electrodes and reproducible electrochemical characteristics, and enables a 30-fold lowering in Pt loading relative to mechanically milled electrodes without loss in activity. For higher temperature fuel cells, Meng reviews in a feature article the state of the art in mechanistic understand of cathode processes and materials development. The authors argue that composite electrodes formed of high-activity mixed oxide-ion and electronic conductors with proton conductors lead to high performance; the first component provides the catalytic activity for oxygen dissociation while its high mobility brings the reactive species to the triple phase boundary at which the reaction occurs. O'Hayre reports a comprehensive model for treating multi-component transport in materials with simultaneous electronic (either hole or electron), oxide vacancy, and proton transport, in contrast to a composite system. A formalism for assessing transport behavior in terms of a ternary plot (analogous to a ternary phase diagram) is presented. In addition, new experimental data show that simultaneous species transport indeed occurs in yttrium doped barium zirconate, resulting, under some conditions, in steam permeation through ceramic membranes. This breadth of activities demonstrates that extensive opportunities remain for bringing the promise of protonics for a clean and sustainable energy future to realization.

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